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Ground state dissociation energies and RKR curves of A state of InI and SrS molecules

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Abstract : The revised spectroscopic constants from the work of Vempati and Jones are used to construct the RKR potential energy curves of X and A states of InI. The Hulbert-Hirschfelder, Lippincott, Tietz and Mattera potentials are used to estimate the D_o values of InI which comes out as 3.41 ± 0.04 eV. The A–X transition of SrS was observed for the first time by Pianalto using the diode laser spectroscopy. Molecular constants yielded from this analysis were used to construct the RKR potential energy curves of X and A states of SrS also. All above potentials were also applied to X state of SrS and the D_o was estimated to be 2.78 ± 0.06 eV.

Keywords : RKRV curve, dissociation energy, diatomic molecular spectra, SrS and InI molecules

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The RKR potential energy curves which decide the shape of the potential energy curves are of importance in the studies of intensity measurements, and the variation of electronic transition moment etc. Dissociation energy is another important parameter in the field of spectroscopy, thermochemistry, chemical physics and astrophysics. One of the methods to estimate the dissociation energy (DE) is to compare the empirical potential function with the RKR [1–3] potential energy curve ; usually known as curve fitting. In the present study the RKR potential energy curves of ground state and excited A state of InI and SrS molecules are constructed. Applying the Hulbert-Hirschfelder [4] (H–H), Lippincott [5], Tietz [6] and Mattera [7] potential functions to the ground states of InI and SrS, their DE's are estimated.

InI was recently studied by Vempati and Jones [8] giving more accurate constants. Estimates of bond dissociation energy of InI kept on changing due to the lack of precise data.

From absorption and fluorescence studies Wehrli and Miescher [9] reported D_0 of InI as 24000 ± 3000 cm^{-1}. Later from flame photometric studies Bulewicz *et al* [10] obtained a value of 25882 cm^{-1}. Vempati and Jones [8] have recently analyzed 11 bands of the AO–XO and B1–XO transitions of InI and reported the vibrational and rotational constants which are reported in Table 1.

Table 1. Molecular constants of A–X transition of InI and SrS.

Molecule	State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	r_e
InI	X	0	176.86	0.33	0.036868	0.000104	2.7545
	A	24403	158.50	1.59	0.38073	0.000237	2.7101
SrS	X	0	388.264	1.2803	0.120803	0.000474	2.4397
	A	13932	339.145	0.5524	0.113989	0.000405	2.5115

All constants are in cm^{-1} except r_e, which are in Å units

Electronic transitions of many diatomic alkaline earth sulfides are reported by Pianalto *et al* [11] using the diode laser spectroscopy. No data for A-state was available prior to this work and therefore it was necessary to calculate the RKR data of $A\,^1\Sigma^+$ state of SrS and also to estimate the DE. Pianalto analyzed 9 bands and derived the molecular constants, which are also listed in Table 1.

The potential functions used are as follows

a) The H–H function :

$$U_H(r) = D_e\left\{\left[1 - \exp(-x)\right]^2 + (1+bx)cx^3 \exp(-2x)\right\}, \tag{1}$$

where

$$x = \left[\omega_e/2(B_eD_e)^{1/2}\right]\left[(r-r_e)/r_e\right];$$

$$c = 1 + a_1\left(D_e/a_0\right)^{1/2}; \qquad b = \left\{2-\left[(7/12) - \left(D_e a_2/a_0\right)\right]/c\right\}.$$

b) The Lippincott function :

$$U_L(r) = D_e\left\{1 - \exp\left[-n(r-r_e)^2/2r\right]\right\}$$

$$\times\left\{1-\left(a^2b^2n/2r\right)(r-r_e)\exp\left[-\left(b^2nr_e/2r^2\right)^{1/2}(r-r_e)\right]\right\}, \tag{2}$$

where

$$\Delta = k_e r_e^2/2D_e; \qquad n/2 = \Delta/r_e;$$

$$a = 0.8 - \left(0.751176/\Delta^{1/2}\right); \qquad b = 1.065.$$

c) The Tietz function :

$$U_T(r) = D_e\left[(r-r_e)/r_e\right]^2\left\{\Delta(1+Q)-Q+(Q/r_e)r\right\}/\left\{1+(Q/r_e)r\right\}, \quad (3)$$

where

$$Q = \Delta(F_e-1)/(2\Delta-\Delta F_e-1) \quad \text{and} \quad F_e = \alpha_e\omega_e/6B_e^2$$

d) The Mattera function :

$$U_M(r) = D_e\left\{1-\left[1+\left(\gamma/pr_e\right)(r-r_e)\right]^{-p}\right\}^2, \quad (4)$$

where

$$p = \left(12a_2-11a_1^2\right)/\left(7a_1^2-12a_2\right); \quad \gamma = -a_1/\left[1+(1/p)\right],$$

a_0, a_1, a_2 are Dunham coefficients and all other notations have their usual meanings.

These potential function were extensively used for calculations of DE's of various diatomic molecules by Bharate *et al* [12–14], Bhartiya *et al* [15] and Bhartiya and Behere [16–18].

The RKR potential energy curves are calculated for the X- and A-states of InI and SrS for the observed vibrational levels *i.e.* $v = 10$ and $v = 8$ levels respectively. The turning points of X-states thus obtained were substituted in different potential functions along with the parameters required which were readily evaluated from the constants in Table 1. U values calculated using potential functions 1–4 were compared with the respective $G(v)$ values which yielded the D_e. These results are presented in Table 2.

Table 2. Comparison of different potentials for the X-states of InI and SrS molecules and the RKR curves of excited states. Energies are in cm^{-1} and r-values are in Å units.

InI v	X-state $G(v)$	r	H–H D_e values 27535	Lippin. derived 28840	Tietz from 27535	Matte. potentials 42043	RKR data of A-state $G(v)$
10	1820.45	2.5314	1833.14	1804.33	1833.74	1833.47	1488.95
9	1650.21	2.5408	1661.43	1639.88	1661.87	1661.69	1362.25
8	1479.31	2.5508	1490.11	1475.12	1490.40	1490.30	1232.37
7	1307.75	2.5616	1317.77	1308.67	1317.95	1317.90	1099.31
6	1135.53	2.5733	1145.40	1141.40	1145.49	1145.49	963.07
5	962.52	2.5862	971.963	972.212	971.980	972.017	823.65
4	789.11	2.6006	798.018	801.557	797.988	798.047	681.05
3	614.91	2.6172	621.987	627.727	621.930	621.998	535.27
2	440.05	2.6368	446.006	452.632	445.943	446.007	386.31
1	264.23	2.6616	269.448	275.351	269.398	269.445	234.17
0	88.35	2.6992	91.1895	94.1451	91.1692	91.1876	78.25
	0	2.7545	0	0	0	0	0

Table 2. (*Contd.*)

InI v	X-state $G(v)$	r	H–H D_e values 27535	Lippin. derived 28840	Tietz from 27535	Matte. potentials 42043	RKR data of *A*-state $G(v)$
0	88.35	2.8117	85.4180	90.7127	85.4011	85.4159	78.25
1	264.23	2.8568	259.507	278.409	259.465	259.499	234.17
2	440 05	2.8892	433.847	468 649	433.789	433.829	386.31
3	614.91	2.9163	607.452	659.756	607.385	607.419	535.27
4	789.11	2.9404	780.973	852 125	780.904	780.921	681.05
5	962.52	2.9624	953.695	1044.75	953.627	953.618	823.65
6	1135.53	2.9829	1125.92	1237.81	1125.86	1125.81	963.07
7	1307.75	3.0023	1298.14	1431.74	1298.09	1298.00	1099.31
8	1479.31	3.0207	1469.15	1625.07	1469.12	1468.97	1232.37
9	1650.21	3.0384	1640.20	1819.12	1640.18	1639.98	1362.25
10	1820 45	3.0554	1810 08	2012 45	1810.08	1809.81	1488.95
SrS v	*X*-state $G(v)$	r	H–H D_e values 25417	Lippin. derived 27631	Tietz from 25310	Matte. potentials 22437	RKR data of *A*-state $G(v)$
8	3207 71	2.2219	3568.77	3611.30	3289.29	3273.99	5842.91
7	2839.93	2.2333	3139.19	3190.11	2906.94	2897.59	2512.59
6	2469.59	2.2457	2711.99	2768.61	2523.97	2519.54	2181.18
5	2096.69	2.2593	2288 73	2348.16	2141.61	2141.05	1848.67
4	1721.23	2.2745	1868.32	1927.37	1758.62	1760.86	1515.04
3	1343.21	2.2921	1446 15	1501.23	1370.43	1374.34	1180.32
2	962.63	2.3127	1033.17	1080.26	986.626	991.038	844.49
1	579.49	2.3391	619.769	653.859	597.527	601.211	507.55
0	193.78	2.3792	209.654	224.094	204.960	206.591	169.51
	0	2.4397	0	0	0	0	0
0	193.78	2.5011	177.959	196.936	180.770	182.211	169.51
1	579.49	2.5507	539.657	604.215	555.978	559.226	507.55
2	962.63	2.5866	896.457	1011.23	932.639	935.991	844.49
3	1343.21	2.6169	1248.38	1416.21	1309.18	1310.83	1180.32
4	1721.23	2.6441	1597.79	1820.89	1687.34	1685.39	1515.04
5	2096.69	2.6689	1940.03	2219.20	2061.55	2054.11	1848.67
6	2469.59	2.6922	2279.34	2615.53	2436.03	2421.10	2181.18
7	2839.93	2.7144	2616.49	3010.39	2811.40	2786.89	2512.59
8	3207.71	2.7356	2949.40	3400.98	3185.12	3148.97	5842.91

The well-known relation between D_e and D_0 is given as $D_o = D_e - (\omega_e/2 - \omega_e x_e/4)$ [19a]. Curves of potential energy *versus* internuclear separation are plotted in Figures 1 and 2

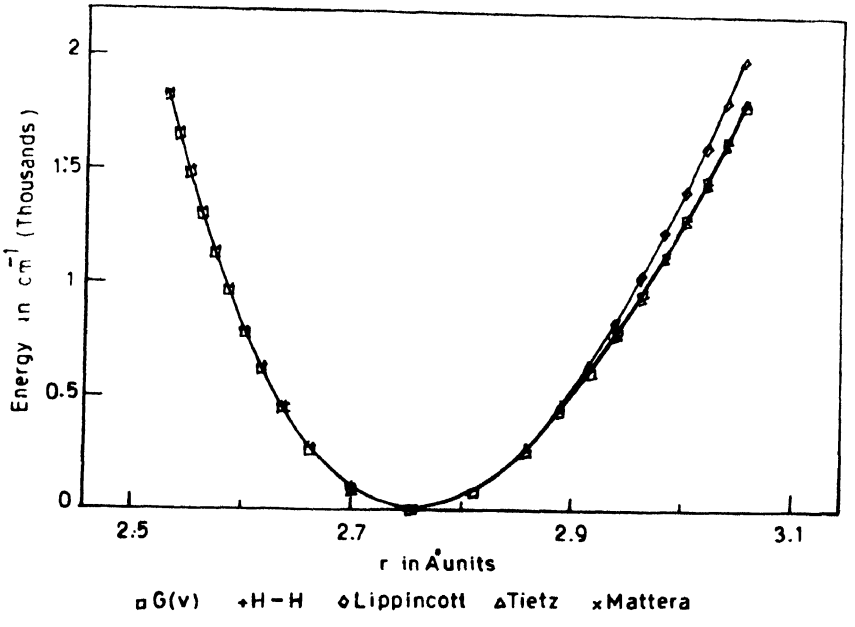

Figure 1. Potential energy curves for the X state of InI.

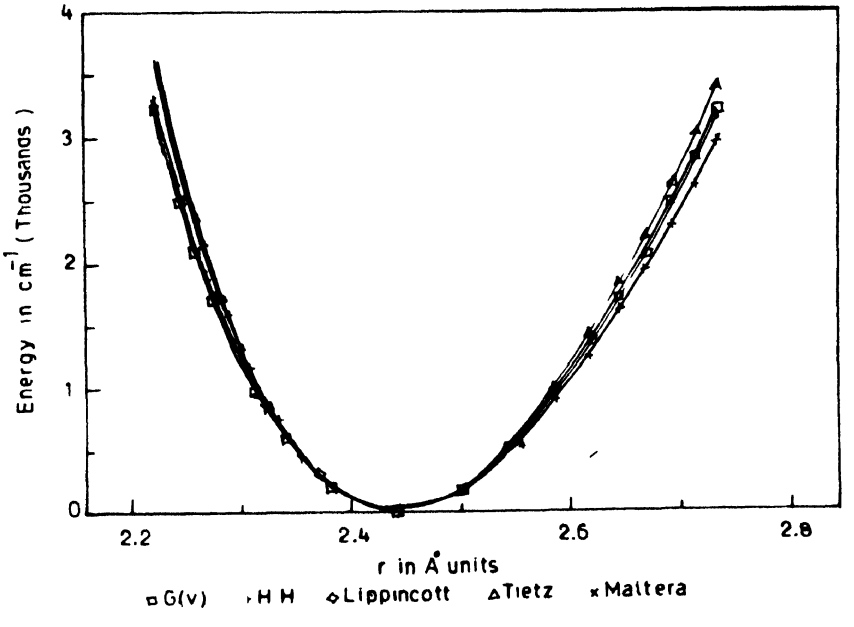

Figure 2. Potential energy curves for the X state of SrS

respectively. In case of InI, the potentials H–H, Lippincott, Tietz and Mattera fit to the RKR curve with D_e values as 27535 ± 342, 28840 ± 7028, 27535 ± 392 and 42043 ± 600 cm^{-1}. This indicates that the H–H and Tietz functions agree well as long as D_e is concerned but although Mattera function can fit to RKR, the higher value of D_e *viz* 40423 cm^{-1} is not acceptable. The Lippincott function deviates from RKR curve because of the large standard deviation. We therefore, choose the H–H function as the better representation to a RKR curve of the X-state of InI. In case of SrS, above potential fit to RKR with D_e values as 25417 ± 2069, 27631 ± 8090, 25310 ± 780 and 22437 ± 697 cm^{-1} respectively. H–H and Lippincott functions show more scatter but the Mattera and Tietz functions show better agreement with RKR curve.

D_e of InI could be taken as 27535 ± 342 cm^{-1} yielded by the H–H function which is in agreement with the recent estimate of 27500 cm^{-1} given by Vempati and Jones [8]. D_0 thus comes as 3.41 ± 0.04 eV for SrS. D_0 reported by Herzberg [19b] is < 2.7 eV. The value reported by Martin and Schaber [20] from mass spectrometric studies is 3.47 eV and rather high. The Mattera and Tietz functions fit to RKR to a better extent. The D_0 is recommended as 2.78 ± 0.086 eV.

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